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POTENTIAL USAGE OF AQUEOUS ALUM FOR DECOMPOSITION OF CHEMICAL WARFARE AGENTS PART 1: REACTIONS WITH V- AND G-TYPE AGENTS

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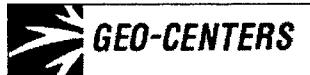
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14. ABSTRACT The objective of this research is to hydrolyze and precipitate G- and V-type CW agents using aluminum sulfate (alum) and/or alum buffer solutions. Soman (GD), O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX), and agent simulants were treated with either aqueous alum, sodium aluminate, or mixtures of the two. Reactions were tracked using ³¹ P nuclear magnetic resonance and gas chromatography/mass spectrometry (GC/MS). A basic alum buffer at pH 12.0 and an acidic alum buffer at pH 3.6 were used for most of the studies. VX was unaffected by the acidic buffer, but GD was eliminated from the aqueous acidic buffer within 18 hr, with nearly 50% removed within the first 10 min. Gas chromatography/mass spectrometry confirmed that, after 24 hr, a chloroform extract of the precipitate formed in this reaction contained < 4 ± 1% of the original GD.					
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PREFACE

The work described in this report was authorized under Project No. 10601384BP0 and Contract No. DAAD13-03-D0017. This work was started in May 2003 and completed in May 2004.

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**POTENTIAL USAGE OF AQUEOUS ALUM
FOR DECOMPOSITION OF CHEMICAL WARFARE AGENTS
PART 1: REACTIONS WITH V- AND G-TYPE AGENTS**

1. INTRODUCTION

Recent attention has focused on the challenges and anxiety associated with the decontamination and disposal of chemical warfare agents (CWA), which is viewed as a potential public health menace.^{1,2} Truly environmentally friendly means of detoxifying chemical warfare agents have yet to be developed, and the possibility of using alum and alum mixtures may be one feasible attractive alternative.

Alum (aluminum sulfate) and alum mixtures have a long history of usage by municipal water treatment facilities as coagulants in the purification and finishing of drinking water. Alum, and alum buffered by the addition of sodium aluminate, have even been used by lake managers for phosphate removal from lakes and reservoirs that were impacted by excess nutrient input giving rise to unwanted algal blooms.³ It was these large scale applications that led us to look further into the possibility of using alum and alum mixtures as alternatives for the decontamination of CWA's, particularly the V- and G-class nerve agents.

The G- and V-type nerve agents hydrolyze under a variety of conditions, and hydrolysis kinetics have been studied for many of these CWA's.^{4,5,6} The pH of alum and alum mixtures can be widely varied from strongly acidic to strongly basic depending on concentrations and proportions of components, which should allow for some control over hydrolysis reaction rates. Thus it was thought that they would have great potential not only in hydrolyzing the agents, but also in rendering the phosphate by-products inactive in the resultant coagulant floc that forms.

The alum approach has several potential applications. For example, it represents an option for insuring the safety of municipal drinking water supplies. In the event that a water supply is contaminated by CW agents in an accidental spill or a terrorist incident, a method may be needed to rapidly decontaminate the water to prevent a risk to public safety. Because alum is already used for water purification, it provides a possibility for decontamination that does not require additional decontamination materials other than those already in use. However, optimization of the treating and filtering conditions may be necessary to purify water, which will require further study. The approach may also be useful for remediation of contaminated manufacturing sites or storage facilities in a way that can immobilize residual CW agent and breakdown products in a nontoxic material.

Here, we report the first installment of an investigation of the potential of using alum and alum mixtures for the destruction of V- and G-type nerve agents. This installment includes work on simulants and agents. Studies were conducted on high

concentrations of agents to facilitate the understanding of the reaction rates and effectiveness of the decontamination.

2. EXPERIMENTAL PROCEDURES

2.1 Materials.

O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX) and soman (GD) were obtained from Aberdeen Proving Ground, MD. The purity of the agents was deemed satisfactory for study based on ^{31}P Nuclear Magnetic Resonance (NMR) spectra obtained in CDCl_3 as described below. All other chemicals were used as obtained (Sigma-Aldrich Co., St. Louis, MO, and subsidiaries) without further purification. Solutions of 1.0 M $\text{Al}_2(\text{SO}_4)_3$, 1.0 M NaAlO_2 , saturated $\text{Al}_2(\text{SO}_4)_3$ (ca. 50% by weight)⁷, and saturated NaAlO_2 (ca. 30% by weight as determined experimentally by C. De Leon and M. Sanders, unpublished data, May 2004, and confirmed by personal communication with M. Schreiber, Sigma-Aldrich Technical Services)⁸ were prepared with deionized water. Unless otherwise noted, all reactions were carried out in 5 mm NMR tubes (507-PP Wilmad Glass, Inc.) in total volumes ranging from 700 to 1000 μL . The total volumes include D_2O added as a lock solvent to give 3 - 30% D_2O by volume.

2.2 Alum Buffer Studies.

Aluminum sulfate (alum)/sodium aluminate buffers were prepared in either 2.0 mL microfuge tubes or 10.0 mL Pyrex test tubes by mixing stock solutions and diluting with water. Two series were prepared: one by combining saturated solutions of the two reagents, another by mixing 1.0 M solutions. All were brought up to a constant total volume, and pH was measured using a Scientific Instruments IQ150 pH Meter fitted with solid state pH probe with internal reference. Volume fractions of alum relative to the sum of alum plus sodium aluminate volumes were then computed and plotted against pH. Table 1 shows the final molar concentration of each component after mixing. The estimated error in reported pH values is ± 0.5 units. Several alum fractions prepared from either saturated or 1.0 M solutions were randomly chosen for dilution experiments in which the amounts of each buffer component and the amount of water were varied while keeping the volume fraction of alum constant.

2.3 ^{31}P NMR Spectra and Gas Chromatographic/Mass Spectrometer (GC/MS) Data.

All nuclear magnetic resonance (NMR) experiments reported are ^{31}P detected, proton inverse gated decoupled. These experiments were collected on samples prepared directly in NMR tubes as described above using a Bruker AVANCE 300 MHz NMR spectrometer fitted with 5 mm broadband probe. All spectra were referenced to external H_3PO_4 (1% (v/v) in D_2O ; 0 ppm). Test solutions were prepared by adding from 20 to 200 μL simulant/agent to NMR tubes already containing D_2O and H_2O . Alum solutions were then added and the reaction components mixed using a

vortex mixer. Spectra were collected on spinning samples (20 Hz) at 121.4 MHz using eight scans with a 60 second delay time between scans. Proton decoupling was accomplished by using the WALTZ16 composite decoupling sequence. All reactions were carried out at ambient temperature (21 - 23° C), and the first spectrum was collected within 1 hr of mixing unless otherwise noted. Chemical shifts are reported in ppm (δ) relative to the external H₃PO₄ standard.

Table 1. Final Molar Concentrations of Al₂(SO₄)₃ and NaAlO₂ in Buffer Solutions

Prepared from 1.0 M Buffer Solutions			Prepared from Saturated Buffer Solutions		
[Al ₂ (SO ₄) ₃]	[NaAlO ₂]	pH	[Al ₂ (SO ₄) ₃]	[NaAlO ₂]	pH
0.00 M	0.50 M	12.9	0.00 M	2.4 M	13.7
0.05 M	0.45 M	11.0	0.06 M	2.2 M	13.2
0.10 M	0.40 M	4.0	0.12 M	1.9 M	12.5
0.15 M	0.35 M	3.8	0.18 M	1.7 M	11.8
0.20 M	0.30 M	3.6	0.24 M	1.4 M	9.2
0.25 M	0.25 M	3.6	0.30 M	1.2 M	4.6
0.30 M	0.20 M	3.5	0.36 M	0.96 M	4.0
0.35 M	0.15 M	3.4	0.42 M	0.72 M	3.7
0.40 M	0.10 M	3.2	0.48 M	0.48 M	3.6
0.45 M	0.05 M	3.0	0.54 M	0.24 M	3.4
0.50 M	0.00 M	1.2	0.60 M	0.00 M	1.2

For these NMR detection conditions, the detection limits were approximately 100 µg/mL for DMMP (8×10^{-4} M) with a signal to noise ratio of 10:1, or a detection limit of 25 µg/mL with a signal to noise ratio of 2.5:1, in a standard solution. If the initial agent or simulant concentration is 20 µL in 1000 µL, then it is possible to detect the analyte until it decreases to 0.1% of the initial concentration. However, this only applies to the analyte that is dissolved in the solvent. If the analyte, or a decontamination product of the analyte that contains phosphorus, is immobilized on the solid precipitate, NMR may not be able to detect it due to signal broadening. As a result, these experiments show the loss of the simulant or agent without a directly corresponding appearance of degradation products, a fraction of which may be immobilized in the solid material.

Gas chromatography/mass spectrometry experiments were carried out on CHCl₃ extracts of the GD agent samples. After the reaction for a particular sample went to completion (based on NMR analysis), the NMR sample was extracted using 0.5 mL of CHCl₃. Samples were analyzed using a JEOL GCmate II mass spectrometer

operated at low mass resolution and 70 eV electron impact ionization. Quantitation was accomplished by comparison with experiments on external standards of soman (GD or 3,3-dimethyl-2-butylmethylphosphono-fluoride) carried out under the same conditions.

2.4 Reaction Rate Experiments.

Timed experiments on simulants/agents to monitor loss of reactant from the solution over time were performed on samples prepared as described above. Values for pH in the reaction rate experiments were not measured directly but estimated based on the alum/sodium aluminate solution composition. Reactivity is reported as the percentage of unreacted simulant/agent as calculated using the ^{31}P NMR peak area relative to either the peak area of an internal standard (hexamethylphosphoramide, HMPA), or relative to the peak area of a blank simulant/agent standard made without the alum buffer added. For each spectrum, the reaction time was taken to be the midpoint of the data acquisition period of 10.2 min. Initial spectra were obtained within the first 15 min after mixing. Error bars represent the 95% confidence limits ($\alpha = 0.025$) based on multiple measurements of peak area.

3. RESULTS AND DISCUSSION

3.1 Alum Buffer Studies.

In setting up the experiments using aluminum sulfate (alum) and sodium aluminate, two stock solution concentrations were chosen, 1.0 M and saturated solutions. We chose 1.0 M solutions to be able to more accurately control the mole fraction of each component added, and saturated solutions to provide excess reagent if needed. In preliminary studies, we noted that combining corresponding solutions (i.e., either saturated or 1.0 M) of the two reagents produced flocculent precipitates as expected based on their usage in water treatment or whole lake treatments.³ Because many hydrolysis reactions of agents are pH dependent, we determined the pH of a series of the alum mixtures (Table 1 and Figure 1). We observed that the saturated solution mixtures and the 1.0 M mixtures demonstrated true buffer behavior in that the pH did not vary over a range of alum:aluminate concentration ratios. Because agent hydrolysis reaction rates depend on pH⁵, ideally the alum buffers could maintain optimal reaction conditions during the process. Saturated solutions are estimated to be about 1.2 M (50% by weight) for alum⁷ and 4.8 M (30% by weight) for sodium aluminate.⁸ Thus, the pH of mixtures prepared from saturated stock solutions tends to lean more heavily toward the basic side relative to the pH of mixtures prepared from 1.0 M buffers.

3.2 Phosphoric Acid and Phosphate Esters.

The original goal behind this research was to determine if alum and alum buffer mixtures could, in addition to hydrolyzing various nerve agents, completely remove the hydrolysis product(s) from solution. Hence, we first analyzed the efficiency

of specific alum mixtures at removing phosphoric acid itself as well as two simple organophosphate esters, triethyl phosphate (TEP) and tributyl phosphate (TBP). Three phosphoric acid samples ($200 \mu\text{L}$) were tested with: 1) $500 \mu\text{L}$ of $1.0 \text{ M Al}_2(\text{SO}_4)_3$, 2) a mixture of $250 \mu\text{L}$ each of $1.0 \text{ M Al}_2(\text{SO}_4)_3$ and 1.0 M NaAlO_2 (to be called "acidic buffered alum" or ABA from here on), and 3) $500 \mu\text{L}$ of 1.0 M NaAlO_2 . The ABA was the only mixture of the three that produced a heavy flocculent precipitate upon mixing. In all three cases, the ^{31}P signal disappeared, indicating the removal of the phosphate species from solution. Each organophosphate ester ($20 \mu\text{L}$) was treated similarly, and Table 2 shows the results. Additionally, TBP and TEP were each treated with a large molar excess of aluminum sulfate by placing $100 \mu\text{L}$ of each simulant into $3000 \mu\text{L}$ of saturated aluminum sulfate solution.

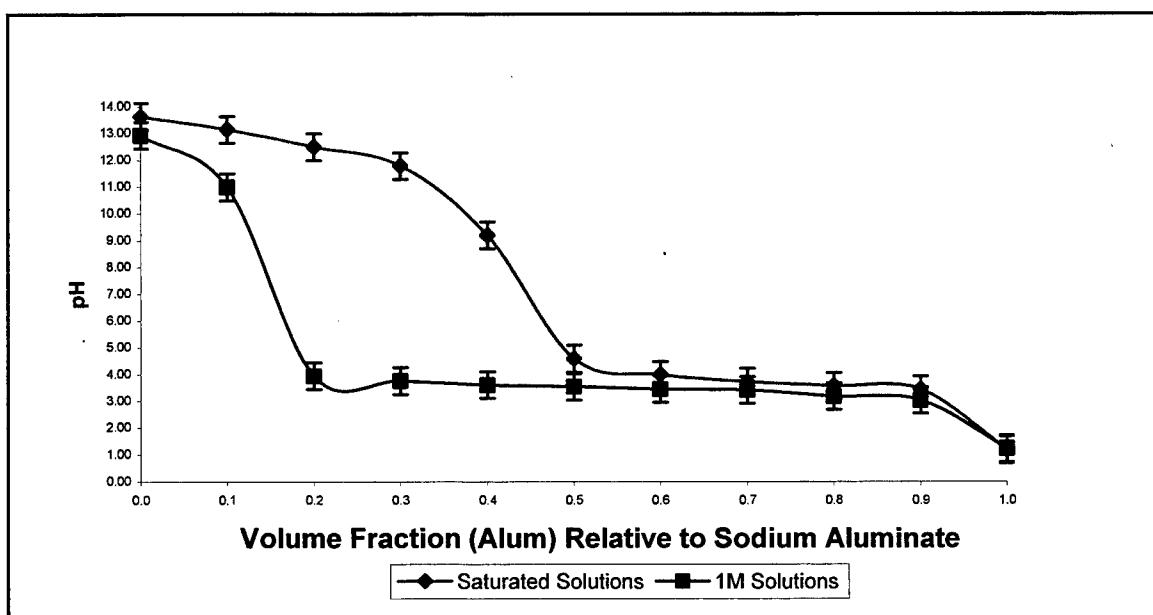


Figure 1. Alum Buffer pH Values as a Function of Volume Fraction for Buffers Prepared from Dilutions of 1.0M (\blacklozenge) or Saturated (\blacksquare) Alum/Sodium Aluminate Stock Solutions

Table 2. Per Cent Simulant Remaining After Addition of Various Alum Mixtures

Simulant	$1.0 \text{ M Al}_2(\text{SO}_4)_3$	1.0 M NaAlO_2	ABA (pH 3.6)	Saturated Alum
H_3PO_4	0	0	0	NT
TEP	$36.6 \pm 0.2^*$	61.1 ± 0.6	72.0 ± 3.8	6.3 ± 0.1
TBP	9.3 ± 0.8	2.5 ± 0.5	0	79.1 ± 1.2
DMMP	NT	NT	48.2 ± 0.2	88.2 ± 3.2
Malathion	See text	See text	See text	See text

*95% confidence limit

NT - not tested

All three of the alum mixtures were expected to remove the phosphoric acid because reactions would result in the precipitation of AlPO_4 in each case. Saturated alum appeared to be the most efficient for removing TEP from solution, but the least efficient for TBP. This may be the result of a combination of ease of hydrolysis and simulant solubility differences in a solution of high ionic strength such as saturated alum. Tributyl phosphate tends to be less soluble in aqueous solutions than TEP.⁷ Our attention was drawn to the ABA solution because of the floc that was formed upon mixing. Despite the fact that it was not as effective for TEP, at least for an immediate reaction, it was effective on TBP and the floc could potentially help entrain by-products as well as unreacted simulants/agents. Thus, this mixture was the one of choice in doing experiments on agents as reported below.

A reaction rate study was carried out on the treatment of TBP with ABA. Figure 2 shows the results of tracking the decomposition of TBP in a solution prepared by adding 100 μL each of 1.0 M $\text{Al}_2(\text{SO}_4)_3$ and 1.0 M NaAlO_2 to 50 μL (ca. 50 mg) simulant in 350 μL of H_2O and 100 μL of D_2O . The more dilute mixture was chosen for two reasons. First, if the reaction mechanism were controlled by the concentration of aluminum in solution, the overall reaction would be slower, thus allowing it to be more easily tracked. Second, it was noted that the precipitate was thicker and more difficult to work with for the more concentrated ABA, especially in a 5 mm NMR tube. The mole ratio of aluminum relative to simulant in the dilute ABA buffer is approximately 1.6:1, and in the more concentrated ABA (reported in Table 2), it is about 10:1.

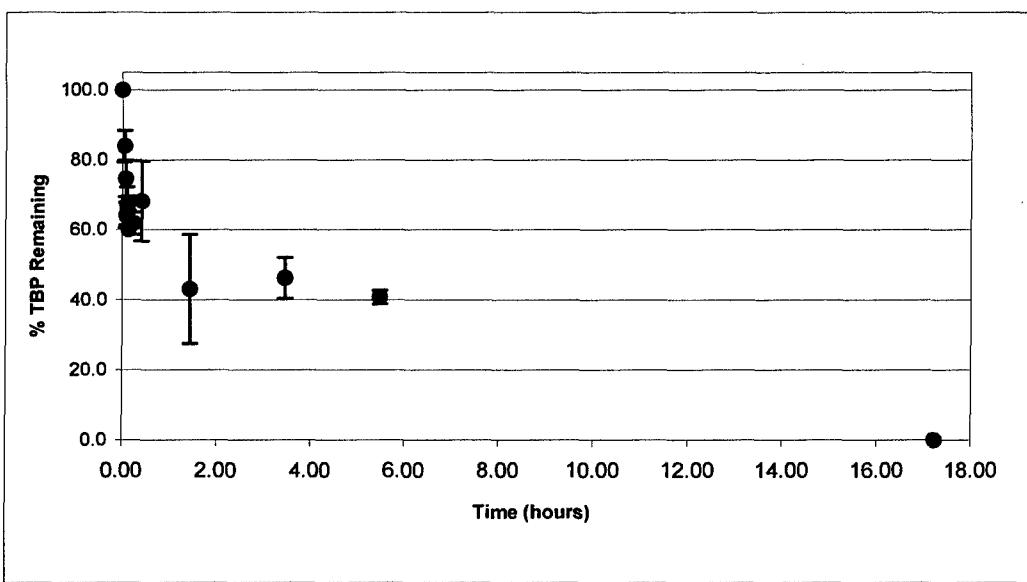


Figure 2. Decomposition of Tributyl Phosphate in Acidic Buffered Alum Solution

As can be seen in Figure 2, the curve does not fit any of the classical kinetic models, which is not surprising because the reaction mixture is very heterogeneous despite the lower concentration of buffer used. Low signal-to-noise ratios in the spectra gave rise to a large variability in the integration values, accounting

for the large error bars. This was the case in all kinetic studies done in NMR tubes with simulant or agent. Issues of incomplete mixing and settling of the precipitate during spinning in the probe made for non-ideal conditions. Nevertheless, it can be seen that despite these challenges, the simulant was totally removed (below detection limits of 0.1%) from solution within 18 hr.

3.3 Phosphonate and Thiophosphonate Esters.

To more closely mimic G-type and V-type nerve agents, two phosphonate esters were studied: O,O'-dimethyl methylphosphonate (DMMP) and malathion (S-[1,2-bis-(ethoxycarbonyl)ethyl]-O,O-dimethylthiophosphate). Although the functional groups are not precisely similar to the nerve agents, these compounds did provide some useful results.

As can be seen in Table 2, the acidic buffered alum solution was more successful in reducing the concentration of DMMP than saturated alum. Subsequent kinetic studies with ABA on DMMP, however, showed no further significant reduction in concentration over time. Work by Brevett and Wagner⁸ shows that DMMP is more effectively hydrolyzed at higher pH. Whether DMMP was actually hydrolyzed and precipitated or simply taken out of solution by surface adsorption to the floc is unknown at this time. Because the alum buffer system has flexibility with regard to pH, we switched to a strongly basic buffer (pH 12.0) prepared from saturated stock solutions. Figure 3 shows the results of a rate study in which the DMMP peak (δ 38.4 ppm) was below detection in approximately 1 hr. Figure 4 shows a sample spectrum recorded approximately 24 min after mixing, in which a second peak has grown in at δ 28.3 ppm (Figure 4). This peak corresponds to sodium O-methyl methylphosphonate (NaMIMP), a basic hydrolysis product.⁸ A shoulder of this peak appeared after 24 hr at δ 26.5 ppm, which corresponds to disodium methylphosphonate (Na₂MP).⁸ In addition to the disappearance of DMMP from solution, the strongly basic alum buffer removes about 50% of all DMMP products over the time frame studied as can be seen in Figure 3.

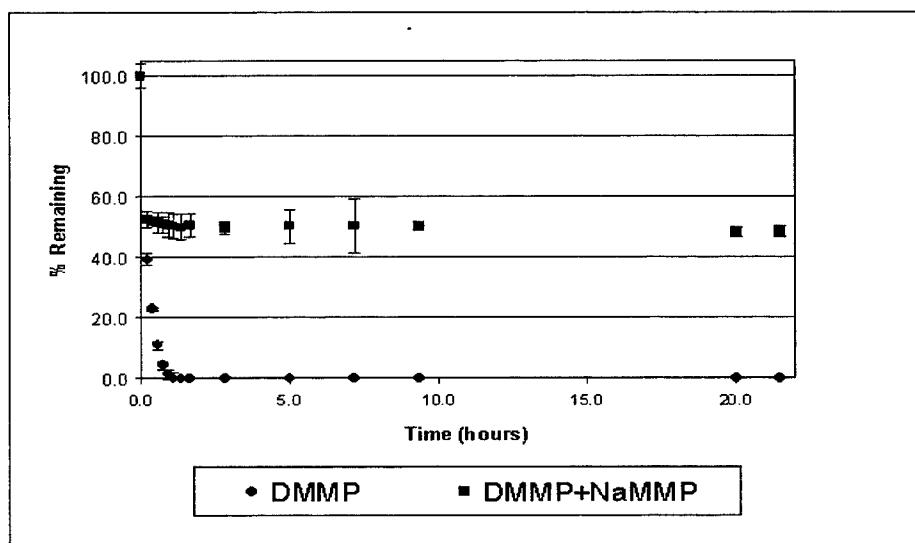


Figure 3. Decomposition of DMMP in Strongly Basic Buffered Alum

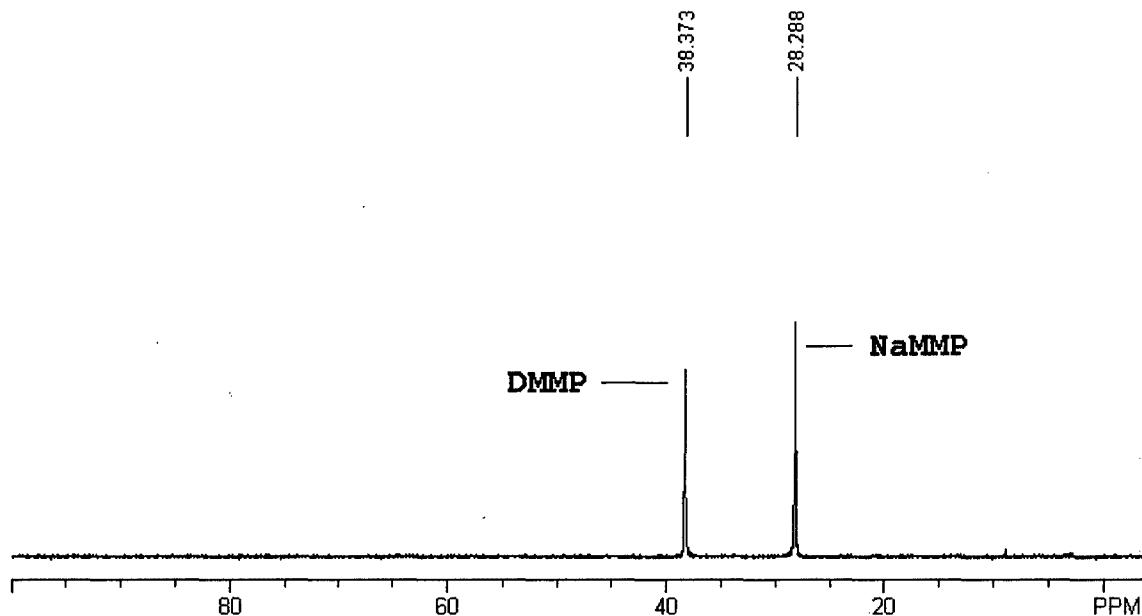


Figure 4. ^{31}P NMR Spectrum of DMMP and Sodium O-Methyl Methyl-phosphonate (NaMMP) 24 min After Mixing with Strongly Basic Buffered Alum

Malathion was apparently untouched by acidic buffer. In fact, the malathion peak at δ 94.9 ppm appeared to increase in intensity relative to the $\text{H}_2\text{O}/\text{D}_2\text{O}$ malathion reference solution without buffer. This would imply that the acidic alum buffer actually increased the solubility of malathion. As an internal standard was not used for this reaction rate experiment, there was no standard for comparison between the malathion reference and the malathion reaction rate samples. The strongly basic buffer also appeared to increase solubility initially, but as can be seen in Figures 5 and 6, the malathion was removed from solution over time. After about 3 hr, two new peaks appeared in the spectrum, one at δ 57.9 ppm and one at δ 115.4 ppm. While the identities of these were not confirmed, based on NMR simulation calculations (ACD, Incorporated), we speculate that the peak observed at δ 57.9 ppm may represent a dithiophosphate ($\text{PO}_2\text{S}_2^{3-}$) derivative (predicted value δ 57.2 ppm). The peak at δ 115.4 ppm may be due to some type of aluminum complex of O,O'-dimethyldithiophosphate. The large downfield shift is within the observed range (δ 105 - 120 ppm) reported for dimeric zinc dialkyldithiophosphate complexes used as anti-oxidants and anti-wear agents in lubricants.⁹ The lack of reactivity of malathion in the acidic buffer may in part be understood by Pearson's Hard-Soft Acid-Base concept (HSAB)¹⁰ where the hard acidic aluminum species have less attraction for the softer sulfur base, and thus hydrolysis and/or precipitation is not favored. For malathion and sulfur-based agents, perhaps a different hydrolyzing/precipitating compound such as iron(III) sulfate may be effective. Not only are most iron phosphate salts insoluble, but there is an additional HSAB feature in that iron tends to associate more strongly with sulfur. There may even be a redox couple involved, with iron(III) oxidizing the sulfur and precipitating it as elemental S. These hypotheses are subjects for future investigation.

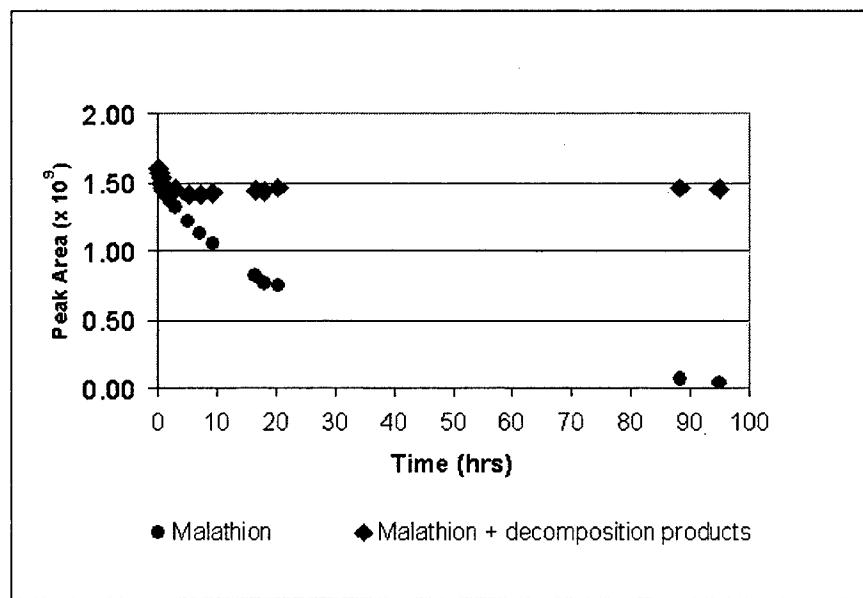


Figure 5. Decomposition of Malathion in Strongly Basic Buffered Alum

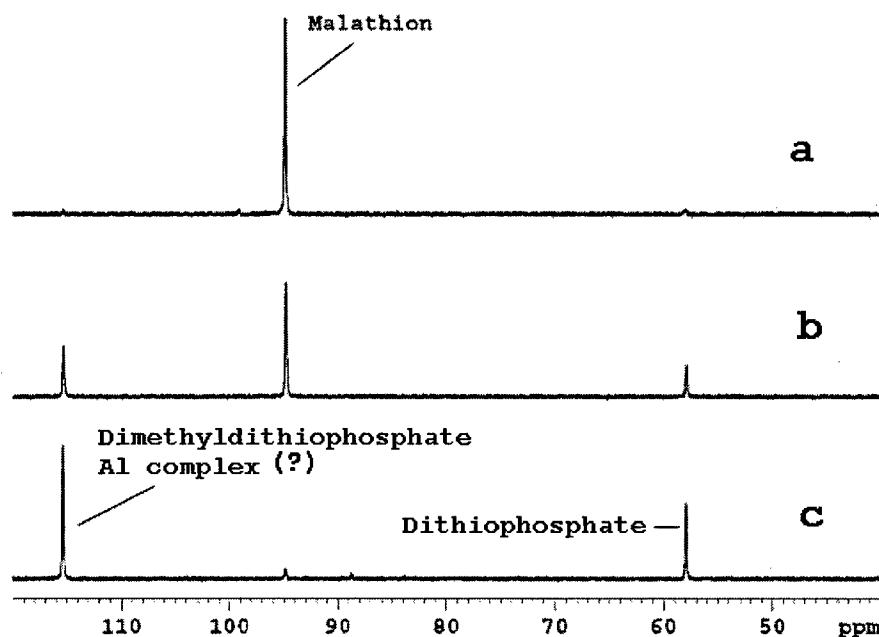


Figure 6. a) ^{31}P NMR Spectrum of Malathion in Strongly Basic Buffered Alum 1 hr After Mixing Showing That Only the Malathion Peak Is Present. b) ^{31}P NMR Spectrum of Malathion in Strongly Basic Buffered Alum 17.5 hr After Mixing Showing Appearance of Decomposition Products (see text). c) ^{31}P NMR Spectrum of Malathion in Strongly Basic Buffered Alum 3.5 Days After Mixing Showing Decomposition Products

3.4

Agent Studies.

Two agents were chosen for study, VX and GD. Both agents were tested with acidic buffered alum only. Two GD experiments were carried out, one with an external standard in water and one with an internal standard of hexamethylphosphoramide (HMPA, 99+% purity from Sigma Aldrich). The results were not significantly different because the addition of ABA did not affect the NMR signal for HMPA. For the GD experiments, 20 mg of GD (purity greater than 95% as determined by NMR) was added to 1 mL of ABA solution. The composite graph of the two time studies is seen in Figure 7. The GD signal was below the NMR detection limit of 0.1% when the last spectrum was recorded around 17.5 hr later.

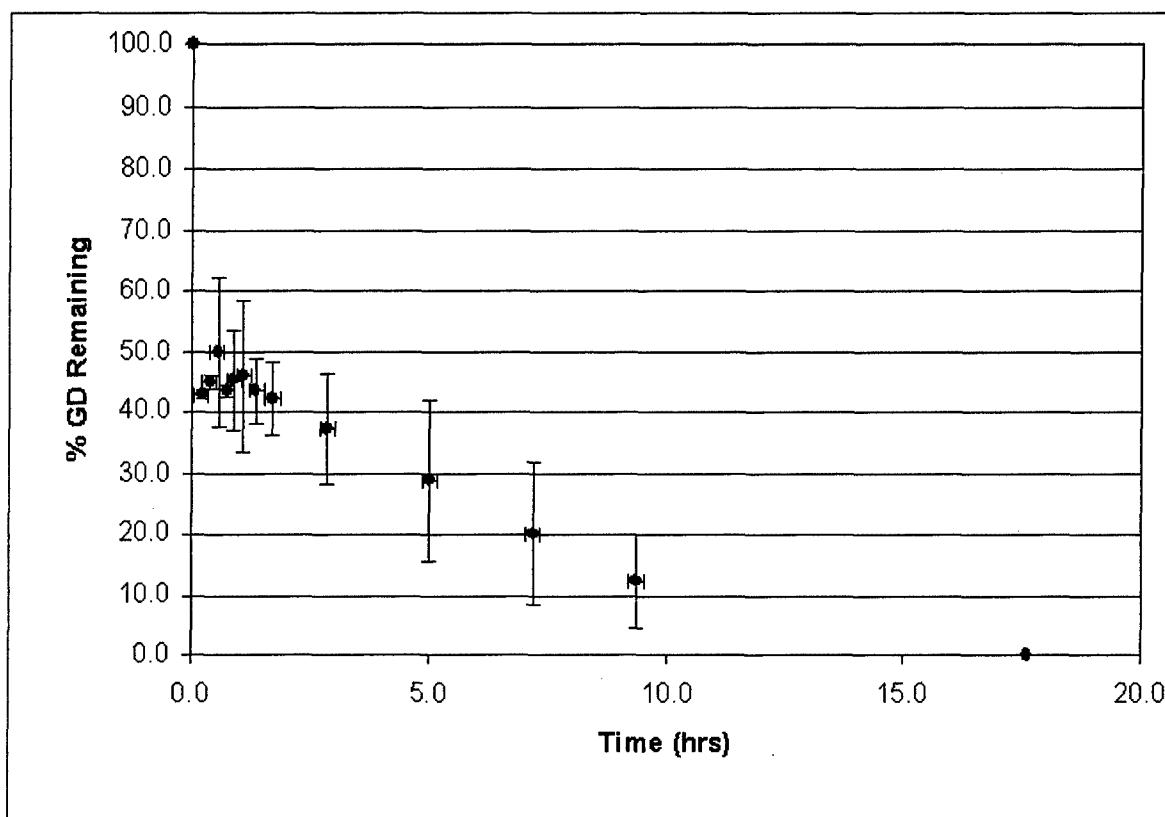


Figure 7. Decomposition of GD in Acidic Buffered Alum Solution

The resulting reaction mass, including solid from the start of the reaction and liquid, was extracted with 0.5 mL of chloroform after 18 hr of reaction. Gas chromatography/mass spectrometry analyses were carried out on the chloroform extracts diluted 1:100 and quantified by comparison to an external GD standard. Results showed that $4\pm1\%$ of the initial GD was recovered by the extraction. Because NMR did not detect this amount of GD in the aqueous solution and GD has a higher solubility in chloroform relative to the high-salt-concentration aqueous solution, it may

be concluded that the GD was extracted from the floc precipitate. Therefore, about 95-97% of the GD was destroyed by conversion into a phosphorus compound that was insoluble in chloroform, but a small amount of the GD was still adsorbed or co-precipitated in the solids. No experiments were done to determine the extraction efficiency of GD from the floc.

On average, about 50% of the GD reacted within the first hour. Figure 8 shows the ^{31}P spectra of GD after 8 min (Figure 8a) and 17.5 hr (Figure 8b, final spectrum recorded). Two fluorine containing species are observed in the initial spectrum (Figure 8a). The initial spectrum shows peaks of both enantiomers of GD (GDa and GDb)¹¹ with an average center around 34 ppm. The second set of enantiomer peaks are centered around 30 ppm, and we assign these to some form of aluminum complex with unhydrolyzed GD. Based on assignments reported by Wagner, et al., the broad peak around 26 ppm at 17.5 hr (Figure 8b) corresponds to pinacolyl methylphosphonic acid (PMPA) while the peaks around 20 ppm are most likely associated with the additional hydrolysis product, methyl phosphonic acid (MPA).¹² No hydrolysis products were identified by GC/MS. This indicates that PMPA and MPA are associated with the floc, probably as surface-bound species given the similarity of chemical shifts to those noted by Wagner, et al.¹² One would also expect that the hydrolyzed fluoride ion may either form HF and/or the very stable hexafluoro-aluminate(III) anion (AlF_6^{3-}) in the presence of excess Al^{3+} ion. As yet, however, this remains unconfirmed.

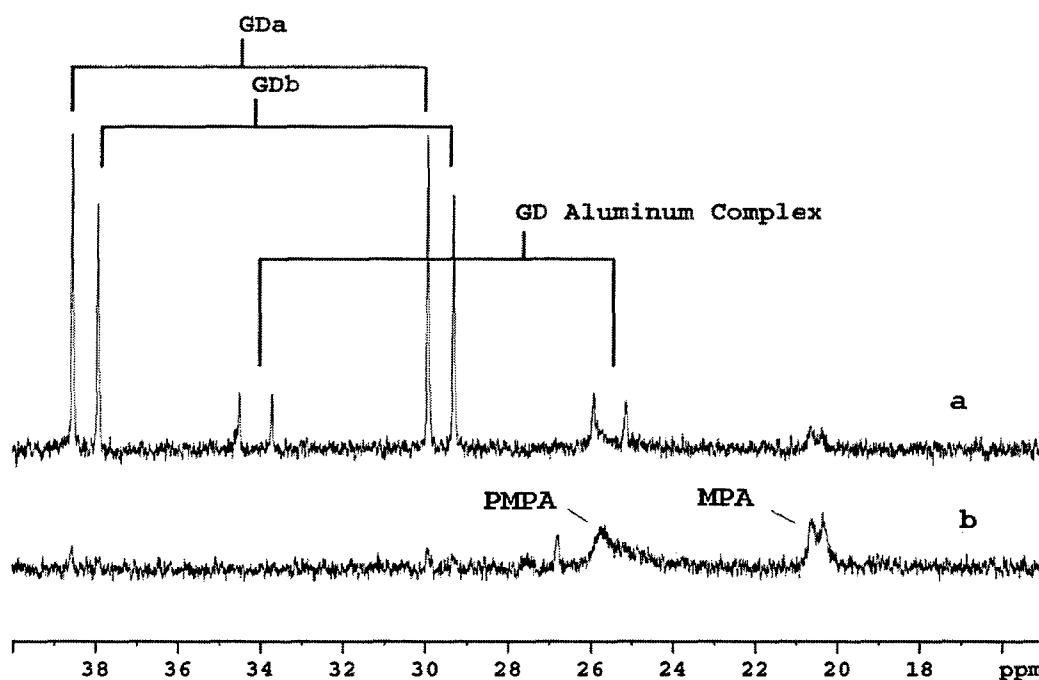


Figure 8. ^{31}P NMR Spectrum of GD Reaction Mixture in Acidic Buffered Alum:
a) 8 min After Mixing, b) 17.5 hr After Mixing Showing PMPA
(ca. δ 26 ppm) and MPA (ca. δ 20 ppm) Peaks

On the other hand, VX responded similarly to malathion in acidic buffer. This time, however, neither internal nor external standards were used for the reaction rate study, so the absolute amount of VX that precipitated in the floc was not determined. Based on the observed reaction of the remaining agent, however, it was evident that the destruction of VX in this solution was not efficient. It was expected that the acidic buffer would be more effective than the basic buffer simply because VX is more soluble in acid than in base.⁴ However, the ³¹P spectrum VX peak at δ 63.3 ppm showed no decrease in size over 24 hr. The acidic floc was therefore ineffective at removing VX from solution. An additional 100 μ L of saturated NaAlO₂ was added to the NMR tube to bring the pH up to what was estimated to be around 12, and the reaction was checked periodically over an additional five days. The final measurement showed a loss of only ~25% of the VX after the addition of NaAlO₂ (Figure 9). Clearly the VX is resistant to either the acidic or basic alum buffer. There was no NMR-observable formation of E2192 in the Acidic Buffered alum or upon raising the sample pH with NaAlO₂.

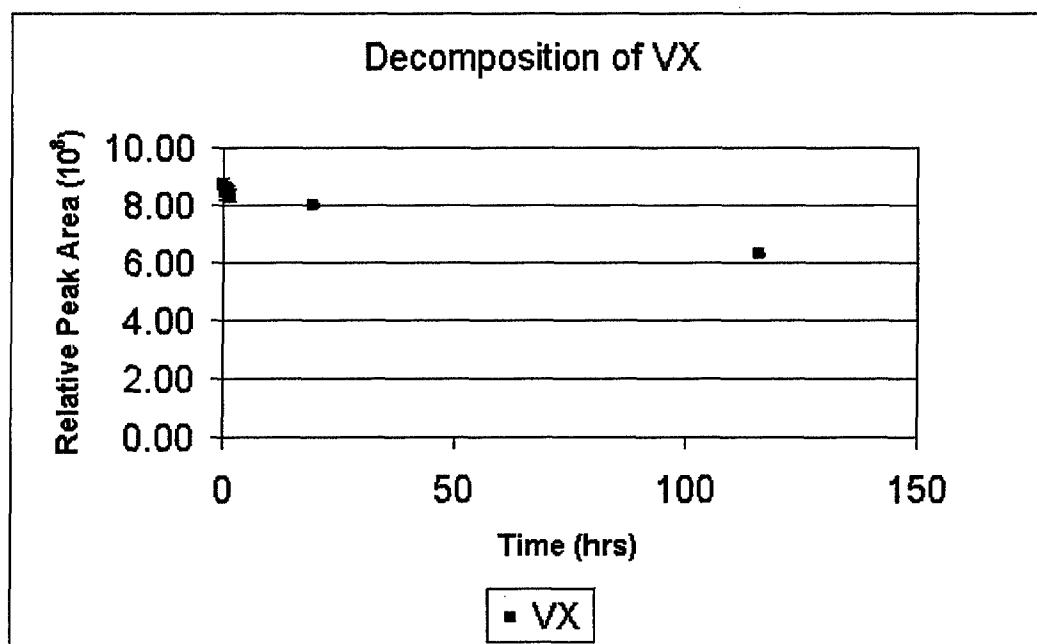


Figure 9. Decomposition of VX in Strongly Basic Buffered Alum

4. CONCLUSIONS AND FURTHER STUDY

These studies have shown that alum buffer mixtures are effective at removing certain phosphoryl-based simulants and nerve agents from water. In addition, the reaction rates of hydrolysis can be controlled to some degree by adjusting the molar ratio of alum relative to simulant/agent. The specific alum mixture used must be optimized for each compound individually if the most efficient removal of that compound and its byproducts is desired. There are still many unanswered questions which need investigation before implementing this technology. Proposed future work with other

G agents will involve identification of decomposition products in the alum floc and supernatant solution because it must be demonstrated that floc and hydrosylate are non-toxic when they are introduced into landfills and waste streams, respectively. Alum buffers had only a marginal affect on VX which is an agent of major concern regarding its destruction.² It is possible that different stoichiometries of alum buffer could prove useful, but an alternate route involving $\text{Fe}_2(\text{SO}_4)_3$ should also be investigated. Nevertheless, we have demonstrated that buffered alum solutions are particularly promising for the decomposition of G agents. This approach may therefore be developed further for stockpile destruction and also to insure the safety of municipal drinking water supplies. Because alum is already used for water purification, optimization of the filtering conditions may be all that is necessary to purify water in the event of water supply contamination by chemical warfare agents in an accidental spill or terrorist incident.

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LITERATURE CITED

1. Greenberg, M.R. Public Health, Law, and Local Control: Destruction of the U.S. Chemical Weapons Stockpile. *Amer. J. Public Health* **2003**, 98(8), pp 1222-1226.
2. Ember, L.R. Destroying Weapons. *C&E News* **2003**, 81(35), pp 26-27.
3. Welch, E.B.; Cooke, G.D. Effectiveness and Longevity of Phosphorus Inactivation with Alum. *J. Lake and Reserv. Manag.* **1999**, 15, pp 5-27.
4. Yang, Y.; Baker, J.A.; Ward, J.R. Decontamination of Chemical Warfare Agents. *Chem. Rev.* **1992**, 92, pp 1729-1743.
5. Yang, Y.; Szafraniec, L.L.; Beaudry, W.T.; Rohrbaugh, D.K.; Procell, L.R.; Samuel, J.B. Autocatalytic Hydrolysis of V-Type Nerve Agents. *J. Org. Chem.* **1996**, 61, pp 8407-8413.
6. Wagner, G.W.; O'Connor, R.J.; Procell, L.R. Preliminary Study on the Fate of VX in Concrete. *Langmuir* **2001**, 17, pp 4336-4341.
7. The Merck Index, 11th Edition; Budavari, S., Ed.; Merck & Co., Inc.: New Jersey, 1989; pp 1514, 1522.
8. Brevett, C.A.S.; Wagner, G.W. *Fate of Nerve Agent Simulants on Concrete Substrates*. Presented at the 45th Rocky Mountain Conference on Analytical Chemistry; Hyatt Regency: Denver, CO, 2003.
9. <http://www.process-nmr.com/liquid-p31%20studies.htm> (accessed March 2004).
10. Hard and Soft Acids and Bases; Pearson, R.G., Ed.; Dowden, Hutchinson, and Ross: Pennsylvania, 1973.
11. Mesilaakso, M.; Niederhauser, A. *Nuclear Magnetic Resonance Spectroscopy in Analysis of Chemicals Related to the Chemical Weapons Convention*. In *Encyclopedia of Chemical Analysis*; R.A. Meyer, Ed.; John Wiley & Sons: England, 2000.
12. Wagner, G.W.; Procell, L.R.; O'Connor, R.J.; Munavalli, S.; Carnes, C.L.; Kapoor, P.N.; Klabunde, K.J. Reactions of VX, GB, GD, and HD with Nanosize Al₂O₃. Formation of Aluminophosphonates. *J. Amer. Chem. Soc.* **2001**, 123, pp 1636-1644.